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Supporting Information

The Use of Tethered Addends to Decrease the Number of Isomers of Bisadduct Analogues of PCBM**

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SUPPLEMENTARY MATERIAL

All reagents and solvents were used as received or purified using standard procedures. [60]-Fullerene (99.5 %) was purchased from Bucky USA and used without further purification. Flash chromatography was performed using silica gel (Kieselgel Merck Type 9385 (230-400 mesh)). ^{1}H NMR and ^{13}C NMR were performed on a Varian Unity Plus (500MHz), on a Varian AMX-400 (400 MHz) or on a Varian VXR-200 (200 MHz) instrument as indicated, at 298 K using TMS as an internal standard, *J* values are given in Hertz. IR measurements were performed on a Nicolet Nexus FT-IR instrument. High Resolution Mass Spectroscopy (HRMS) was performed on a JEOL JMS 600 spectrometer. HPLC analyses were performed on a Hewlett Packard HP LCChemstation 3D (HP 1100 Series) using an analytical Cosmosil Buckyprep. column (4.6 x 250 mm) or a Chrompak silica column (3 x 250 mm) Elemental analysis was performed by the Micro Analytical Department of this laboratory.

4-benzoyl butyric acid (1). A 5 L flask equipped with mechanical stirrer and placed in an ice water bath was charged with 500 ml toluene-free benzene and 512 g $AlCl_3$. A solution of 192 g glutaric anhydride (1.68 mol) in 300 ml 1,2-dichloroethane was made, filtered, and loaded in a dropping funnel. The solution was added over period of 2.5 hours to the benzene under vigorous stirring. The reaction mixture changed from colourless to yellow, to red, to almost black. The mixture was stirred overnight allowing it to slowly warm up to room temperature. The resulting slurry was poured on ice and extracted with ethyl acetate. The organic fraction was collected and evaporated to dryness *in vacuo* to remove the remaining benzene and 1,2-dichloroethane. The crude product was redissolved in ethyl acetate and washed with water. The organic layer was collected and extracted with a KOH/water solution. The aqueous layer was the acidified with HCl and the product was extracted with ethyl acetate. The organic layer was washed two more times with water, followed by brine and dried on Na_2SO_4. The solvent was removed *in vacuo* yielding 260 g crude product. Recrystalisation from hot toluene yielded the pure acid as white crystals (205 g, 63%). d_H (400 MHz, $CDCl_3$, Me_4Si) 7.67 – 7.53 (2 H, m), 7.41 – 7.18 (1 H, m), 7.18 – 7.03 (2 H, m), 2.71 (2 H, td, *J* 7.3, 2.3), 2.04 (2 H, td, *J* 7.2, 2.2), 1.91 – 1.46 (2 H, m); d_C (101 MHz, $CDCl_3$, Me_4Si) 199.48, 175.05, 136.74, 133.03, 128.58, 127.90, 37.50, 33.16, 19.34. mp 127.4^{o}C, lit.: 126-128^{o}C.

Keto ester 2. A flame dried 250 ml three-neck flask, equipped with stirring bar and Dean Stark setup, was charged with 10.0 g 4-benzoylbutyric acid (52.0 mmol), 1.4 ml ethylene glycol (0.5 eq.), and 100 ml toluene. A few drops of concentrated sulphuric acid were added. The resulting suspension was heated to reflux temperature and stirred overnight. Upon heating a clear solution was formed. The solution was cooled to room temperature and the solvent was removed *in vacuo*. Pure product was obtained after column chromatography (SiO_2, petroleum ether 40-60/ethyl acetate 2:1), followed by recrystalisation from diethyl ether. Keto ester **2** (9.0 g, X%) was obtained as a white solid. (Found: C, 70.2; H, 6.45. Calc. for $C_{24}H_{26}O_6$: C, 70.2; H, 6.4%); d_H (400 MHz, $CDCl_3$, Me_4Si) 8.01 – 7.92 (4 H, m), 7.55 (2 H, ddd, *J* 6.7, 2.5, 1.3), 7.49 – 7.39 (4 H, m), 4.30 (4 H, d, *J* 1.0), 3.05 (4 H, t, *J* 7.1), 2.45 (4 H, t, *J* 7.2), 2.07 (4 H, p, *J* 7.1); d_C (101 MHz, $CDCl_3$ Me_4Si) 199.48, 173.21, 136.99, 133.31, 128.82, 128.21, 62.34, 37.55, 33.35, 19.43; *m/z* (ESI) 433.16187 (M+Na. $C_{24}H_{26}O_6Na$ requires 433.16271), mp 63.6^{o}C.

Bis-tosylhydrazone 3. A flame dried 250 ml three-neck flask, equipped with stirring bar and Dean Stark apparatus, was loaded with 7.0 g keto ester **2** (17.1 mmol), and 7.0 g tosylhydrazide (2.2 eq.) in 100 ml toluene. The resulting mixture was heated to reflux temperature and stirred overnight. Upon heating a clear solution was formed. The solution was cooled to room temperature. White solids precipated from the solution upon cooling. The solids were filtered off and placed in a vacuum oven overnight for drying (11.2 g, 88%). (Found: C, 61.45; H, 5.7; N, 7.2. Calc. for $C_{38}H_{42}N_4O_8S_2$: C, 61.1; H, 5.7; N, 7.5%); d_C (101 MHz, $CDCl_3$) 174.37, 154.18, 144.06, 136.37, 136.07, 129.76, 128.67, 128.18, 126.46, 63.14, 32.66, 26.11, 21.83, 21.10; *m/z* (ESI) 769.23279 (M+Na requires 769.23418), mp 144.8-154.2^{o}C (decomposition at slightly higher temperature).

Tethered C_{60} bis-adduct 4. Bis-tosylhydrazide **3** (0.5g, 0.69 mmol) was dissolved in 50 ml pyridine in a flame dried 2L flask under inert atmosphere. 0.22 ml 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added (1.47 mmol, 2.1 eq) and the resulting mixture was stirred for 30 minutes. A solution of 0.5 g C_{60} (0.69 mmol) in 500 ml ortho-dichlorobenzene (ODCB) was added together with an additional 500 ml ODCB. The resulting solution was heated with aid of a heat-gun in 15 minutes to 82^{o}C and overnight illumination with a 150W sodium lamp was started.

The mixture was concentrated *in vacuo* and purified by column chromatography (SiO2, toluene). After removal of the eluent *in vacuo* a dark solid remains. The solid was precipitated from ortho-dichlorobenzene in pentane and subsequently centrifuged. The remaining red pellet was washed twice with pentane and dried in a vacuum oven at 40^{o}C overnight. Yielding 183 mg red brown solid (0.17

mmol, 25%). d_H (500 MHz, CS_2 with D_2O inlet, Me_4Si) 8.00-7.15 (broad signals 10H, phenyl rings), 4.72-3.87 (broad signals, 4H, ethylene tether), 3.47-0.95 (broad signals, 12H, -CH_2's); d_C (126 MHz, CS_2 with D_2O inlet, Me_4Si) 169.15, 169.07, 168.90, 168.81, 168.75, 168.72, 168.66, 168.42, 168.33, 149.32, 148.30, 148.23, 147.86, 147.67, 147.05, 146.84, 146.62, 146.01, 145.49, 145.15, 145.06, 145.02, 144.97, 144.91, 144.74, 144.62, 144.59, 144.30, 144.26, 144.15, 144.02, 143.98, 143.80, 143.77, 143.74, 143.70, 143.66, 143.60, 143.52, 143.48, 143.41, 143.34, 143.27, 143.16, 143.12, 143.05, 143.01, 142.96, 142.90, 142.82, 142.79, 142.63, 142.56, 142.49, 142.42, 142.39, 142.31, 142.25, 142.22, 142.15, 142.07, 142.01, 141.96, 141.93, 141.85, 141.77, 141.61, 141.57, 141.53, 141.45, 141.36, 141.34, 141.30, 141.22, 141.16, 141.08, 141.02, 140.96, 140.87, 140.84, 140.77, 140.65, 140.40, 140.36, 140.27, 140.07, 139.99, 139.83, 139.76, 139.66, 139.59, 139.56, 139.41, 139.34, 139.29, 139.23, 139.21, 139.00, 138.90, 138.79, 138.75, 138.65, 138.62, 138.54, 138.42, 138.21, 138.13, 137.90, 137.20, 137.14, 136.56, 136.44, 136.30, 135.44, 135.36, 135.24, 135.15, 135.07, 134.96, 134.85, 134.56, 134.48, 134.35, 134.26, 133.94, 133.85, 133.76, 133.72, 133.40, 133.30, 133.16, 132.94, 132.75, 132.12, 131.21, 130.84, 130.75, 130.29, 129.86, 129.77, 129.65, 129.31, 129.14, 128.86, 128.43, 128.23, 128.10, 126.77, 126.71, 126.30, 126.20, 126.05, 125.94, 125.92, 125.87, 125.83, 125.44, 125.28, 124.58, 123.19, 78.57, 77.86, 77.65, 77.02, 76.71, 75.48, 75.28, 75.12, 75.02, 74.86, 74.80, 74.11, 73.96, 73.42, 72.66, 71.97, 60.87, 60.64, 60.47, 60.10, 60.03, 59.80, 59.54, 59.33, 59.27, 51.12, 47.54, 47.04, 46.94, 46.62, 45.45, 45.36, 44.98, 42.98, 32.60, 32.22, 32.08, 31.81, 31.61, 31.15, 30.95, 30.83, 30.77, 30.60, 30.43, 30.30, 30.19, 30.03, 29.86, 28.81, 28.68, 28.38, 27.99, 27.69, 23.24, 21.28, 21.21, 20.72, 20.23, 19.81, 19.76, 19.60, 19.50, 18.96, 18.61, 12.54, *m/z* (ESI) 1098 (M^- requires 1098).

C_{60} bis-adduct 5 (tbis-PCBM). Tethered bis-adduct **4** was dissolved in 100 ml ortho-dichlorobenzene along with 10 ml methanol and a catalytic amount of concentrated sulphuric acid and stirred for 5 days. The reaction mixture was stripped of solvent *in vacuo,* redissolved in toluene, and purified by column chromatography (SiO_2/toluene). Precipitation from ortho-dichlorobenzene in methanol and subsequent washing with methanol yielded the pure bis methyl ester **5** as a red-brown solid. d_H (500 MHz, CS_2 with D_2O inlet, Me_4Si) 8.00-7.15 (broad signals 10H, phenyl rings), 3.80-3.67 (broad signals, 3H, methyl esters), 2.90-1.62 (broad signals, 12H, -CH_2's); d_C (126 MHz, D_2O) 171.84, 171.68, 171.60, 171.47, 171.42, 170.82, 151.92, 151.67, 150.66, 150.57, 150.36, 149.80, 149.74, 149.43, 149.15, 148.71, 148.22, 147.57, 147.53, 147.45, 147.41, 147.30, 147.26, 147.14, 147.09, 146.85, 146.79, 146.72, 146.68, 146.66, 146.59, 146.39, 146.25, 146.21, 146.15, 146.13, 146.10, 146.07, 146.05, 146.04, 146.00, 145.94, 145.91, 145.87, 145.84, 145.82, 145.76, 145.71, 145.68, 145.55, 145.53, 145.41, 145.37, 145.35, 145.33, 145.28, 145.22, 145.21, 145.17, 145.15, 145.04, 145.01, 144.97,

144.95, 144.86, 144.84, 144.77, 144.72, 144.68, 144.66, 144.65, 144.63, 144.60, 144.58, 144.55, 144.48, 144.45, 144.43, 144.39, 144.35, 144.31, 144.26, 144.23, 144.16, 144.08, 144.03, 144.00, 143.98, 143.91, 143.89, 143.86, 143.83, 143.76, 143.74, 143.71, 143.64, 143.55, 143.52, 143.44, 143.40, 143.39, 143.31, 143.18, 143.08, 142.81, 142.76, 142.71, 142.66, 142.61, 142.55, 142.39, 142.22, 142.17, 142.05, 142.01, 141.93, 141.79, 141.68, 141.66, 141.59, 141.42, 141.38, 141.31, 141.20, 141.10, 141.01, 140.98, 140.94, 140.86, 140.82, 140.41, 139.76, 139.64, 139.49, 139.18, 139.12, 138.95, 137.65, 137.63, 137.24, 137.18, 137.07, 136.94, 136.85, 136.80, 136.70, 136.64, 136.44, 136.17, 136.11, 135.93, 135.91, 135.81, 135.79, 135.58, 135.51, 135.12, 133.57, 133.16, 133.08, 132.16, 132.13, 132.09, 132.03, 131.83, 131.60, 131.35, 131.24, 130.63, 129.79, 128.64, 128.59, 128.55, 128.52, 128.46, 128.35, 128.31, 128.30, 128.29, 128.23, 128.20, 128.16, 128.14, 127.68, 80.60, 80.54, 80.24, 80.03, 79.07, 78.77, 78.46, 78.24, 78.12, 78.00, 77.86, 76.42, 75.25, 75.19, 74.49, 74.40, 61.95, 53.74, 51.20, 51.17, 51.15, 51.14, 51.12, 50.81, 49.46, 49.43, 49.33, 48.96, 48.86, 47.69, 47.46, 47.34, 34.63, 34.30, 34.16, 33.98, 33.78, 33.77, 33.71, 33.58, 33.49, 33.46, 33.44, 33.28, 32.77, 32.54, 30.35, 23.12, 23.02, 22.80, 22.68, 22.58, 22.43, 22.40, 22.36, 21.79, 20.19, , *m/z* (ESI) 1100 (M^- requires 1100).

Single-point energies of the PM3-optimized lowest-energy geometries of the tethered bis-adduct isomers 4

Molecular Modeling was done using the Hyperchem 7.5 professional software package. A first geometry optimalisation was done using the Molecular Mechanics MM+ force field method. These geometries were taken as the starting points for the PM3 semi-empirical geometry optimalisation. A single-point energy was then calculated for each of the geometry-optimized lowest-energy stereoisomers.

Table S1: Single-point energies of the PM3-optimized lowest-energy geometries of the tethered bis-adduct isomers **4**.

Isomer	Orientation*	relative energy (Kcal/mol)
Cis 1	Exo/exo	19.7
Cis 1	Endo/exo	24.8
Cis 1	Endo/endo	30.9
Cis 2	Exo/exo	1.2
Cis 2	Endo/exo	0
Cis 2	Endo/endo	0.8
Cis 3	Endo/exo	5.2
Cis 3	Exo/exo	8.8
Cis 3	Endo/endo	44.1
E	Endo	19
E	Exo	0
Trans 4	Endo/exo	14.9
Trans 4	Endo/endo	38.5
Trans 4	Exo/exo	24.3
Trans 3	Exo/exo	13.5
Trans 3	Endo/exo	6.6
Trans 3	Endo/endo	38.4
Trans 2	Exo/exo	29.9
Trans 2	Endo/exo	83.1
Trans 2	Endo/endo	Too high
Trans 1	Exo/exo	135.8
Trans 1	Endo/exo and endo/endo	Too high

* “Exo/exo” meaning both phenyl groups are pointing away from each other and both the esters groups towards each other. “Endo/exo” meaning one of the phenyl rings is pointing toward an ester group. “Endo/Endo” meaning both the phenyl groups are pointing towards each other and the ester groups away from each other. “Endo” meaning the phenyl group is pointing towards the second addend. “Exo” meaning the phenyl rings is pointing away from the second addend.

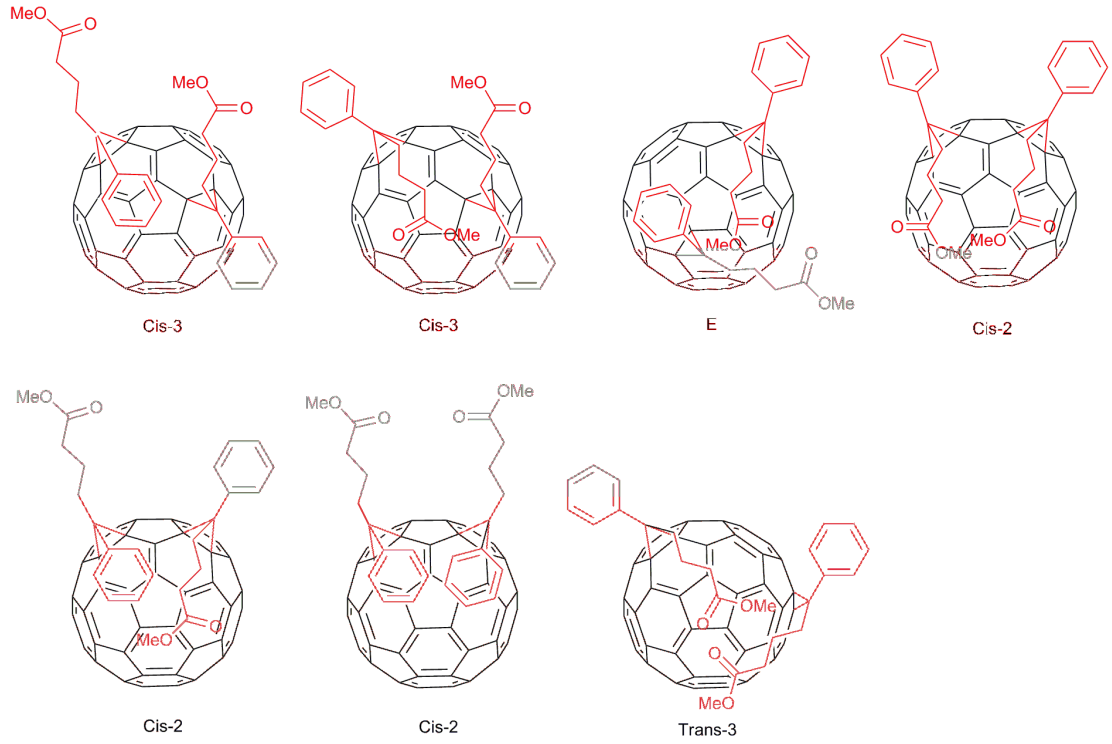

Figure S1: The seven proposed isomers in the tbis-PCBM mixture.

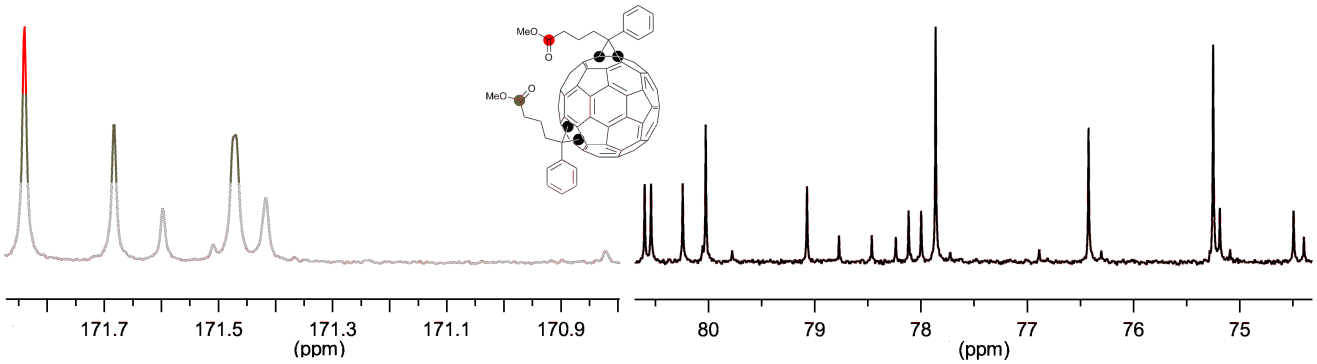

Figure S2: Colour version of Figure 1: The ^{13}C NMR spectrum of the carbonyl (left) and bridgehead (right) area of the isomers obtained from tethered addends.